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<b>(21) International Application Number:</b> PCT/IL00/00261 <b>(22) International Filing Date:</b> 7 May 2000 (07.05.00)  <b>(30) Priority Data:</b> 60/132,813                      6 May 1999 (06.05.99)                      US  <b>(71) Applicant (for all designated States except US):</b> MPM LTD. [IL/IL]; 11 Yohanan Hasandlar, Haifa Bay, 32962 Haifa (IL).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> LEVIN, Ludmila [IL/IL]; 13 Hazait Street, 27000 Kiriath Bialik (IL).  <b>(74) Agent:</b> EITAN, PEARL, LATZER & COHEN-ZEDEK; 2 Gav Yam Center, Shenkar Street 7, 46725 Herzlia (IL).		<b>(81) Designated States:</b> AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> MAGNETIC POLISHING FLUIDS  <b>(57) Abstract</b> <p>Magnetic polishing fluid (MPF) compositions comprising various size colloidal and/or non-colloidal magnetic particle and colloidal size polishing particle compositions suitable for polishing ceramic and glass substrates are described. The compositions are usually aqueous compositions having very basic pHs. Magnetic polishing fluid compositions for polishing metal substrates containing colloidal and/or non-colloidal magnetic particles are also described. These latter compositions contain oxidizers and, usually, oxidation inhibitors for assisting in the polishing process. The MPFs usually include colloidal polishing particles. MPF compositions for polishing metals are usually highly acidic aqueous compositions. Methods for preparing the various MPF compositions are described.</p>		

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## MAGNETIC POLISHING FLUIDS

### FIELD OF THE INVENTION

5 The present invention relates to magnetic polishing fluids for polishing ceramic or optical materials. The present invention also relates to magnetic polishing fluids useful for polishing metallic surfaces, particularly metal surfaces used in the microelectronic industry.

### BACKGROUND OF THE INVENTION

10 Chemical-mechanical polishing is a commonly used technique for planarization of bare silicon, silica and other ceramic wafers. In chemical-mechanical polishing, the wafers are held against a rotating polishing pad wetted by a slurry consisting of colloidal abrasive particles (silicon dioxide, alumina, cerium oxide, etc.) and specific additives to enhance the rate and  
15 quality of polishing. When silica is used, a high pH is required. An oxide or hydroxide surface layer forms on the wafer and the reaction products are removed by mechanical action of the pad and the colloidal silica slurry. Similar processes occur when other abrasives are used.

The bending and stresses of the rotating polishing pad strongly influence  
20 the quality of planarization. The adverse effects of a solid polishing pad can be avoided, or at least mitigated, by using a magnetic polishing fluid which forms a plasticized mass in an inhomogeneous magnetic field.

Magnetorheological fluids (MRFs) for polishing are known in the art. Typical MRFs are described in US Patent Nos. 5,449,313, 5,525,249,  
25 5,795,212, 5,804,095 and 4,921,466. With MRFs, the polishing pad common to conventional polishing is dispensed with entirely.

The viscosity of magnetorheological fluids increases in a magnetic field and the fluids, which contain magnetic particles, acquire the characteristics of a plasticized solid, forming an abrasive mass with a viscosity and elasticity  
30 suitable for polishing.

Polishing machines used with prior art MRF compositions cause the MRFs to acquire viscous, plasticized properties known as Bingham properties,

when the fluids are subject to the influence of magnetic forces. When in a magnetic field, the MRF is hard enough to be used as a polishing tool. However, these polishing fluids reach their fully developed Bingham state only at the outset of the polishing process. Once the substrate being polished begins to move relative to the MRF, the shear stress of the abrasion process causes the MRF to lose its Bingham properties and its plasticized characteristics. The MRF remains viscous throughout the process but returns to a liquid, non-plasticized state almost immediately after abrasion begins, thereby reducing polishing efficiency.

The magnetorheological fluids in the above-cited compositions usually do not provide a chemical mechanism for enhancing the efficiency of the polishing process. In addition, these fluids generally contain magnetic and/or abrasive particles with sizes in excess of 1  $\mu\text{m}$ . These large size particles, and especially their agglomerates, introduce defects, scratches and non-uniformities onto the surface being treated.

Finally, because of the large size magnetic or abrasive particles used, these fluids have a tendency to settle due to gravitational forces. Because of their size, the abrasive particles act as agglomeration centers, contributing to the aggregation of magnetic particles and to the instability of the magnetic fluid.

Any use of such fluids requires prior agitation.

Copper interconnects in ultra-large scale integrated (ULSI) circuit layouts were introduced relatively recently into the semiconductor industry. They became possible as a result of improvements in chemical-mechanical planarization (CMP) technology developed during the last two decades. The adoption of CMP for polishing or removing thin metal layers, such as copper, aluminum, tungsten, titanium and tantalum layers, has enabled their commercial use and markedly changed semiconductor processing.

The use of CMP has led to a large increase in the amount of metal being polished in the semiconductor industry. Only ten years ago, the polishing of dielectric ceramics constituted more than 90% of semiconductor material polished. The current volume of metal being polished in the industry exceeds by several hundred percent that polished formally. The CMP techniques presently

used for metals are very similar to those used for polishing ceramics described above.

The bending and stresses of the rotating polishing pad used in conventional CMP polishing, strongly influence the quality of planarization. As with the other types of substrates discussed above, the adverse effects of a polishing pad on the polishing of metal surfaces can be avoided, or at least mitigated, by using magnetic polishing fluids.

The above-cited references when mentioning polishing, do so only in the context of polishing ceramic or optical materials. They do not discuss polishing metal surfaces.

### SUMMARY OF THE INVENTION

The present invention discusses magnetic polishing fluid compositions and their methods of preparation. These compositions can be used in polishing many different types of materials found in the semiconductor, optical and microelectronic industries. In particular, they can be used to polish ceramics, metalloids and glass surfaces.

The present invention also relates to magnetic polishing fluid compositions suitable for polishing metal surfaces. In particular, it is suitable for polishing metal interconnects, vias and layers used extensively in current ULSI manufacturing.

The present invention teaches various magnetic polishing fluid compositions. One embodiment of such a composition includes colloidal size magnetic particles where the mean particle size ranges from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ , colloidal size polishing particles where the mean particle size ranges from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ , at least one stabilizer and a carrying fluid where the pH of said composition is in excess of 9.

Another magnetic polishing fluid embodiment comprises colloidal and non-colloidal magnetic particles, where the non-colloidal magnetic particles have a mean particle size ranging from about 0.15  $\mu\text{m}$  to about 3.0  $\mu\text{m}$  and the colloidal magnetic particles have a mean particle size ranging from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ . The composition includes colloidal size polishing particles

which have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$  and at least one stabilizer for stabilizing the colloidal size particles. Finally, the composition contains an additive for adjusting viscosity, and a carrying fluid wherein the pH of said composition is in excess of 9.

5 A third magnetic polishing fluid embodiment comprises magnetic particles with a mean particle size ranging from about 0.15  $\mu\text{m}$  to about 3.0  $\mu\text{m}$ , colloidal size polishing particles with a mean particle size ranging from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ , at least one stabilizer for stabilizing said colloidal particles, an additive for adjusting viscosity, and a carrying fluid where the pH of said  
10 composition is in excess of 9.

The invention teaches a method for preparing a composition comprising the steps of preparing a colloidal size magnetic particle dispersion with a stabilizer in a carrying fluid, preparing a colloidal size polishing particle dispersion in a carrying fluid, mixing said colloidal size magnetic particle  
15 dispersion and said colloidal size polishing particle dispersion to form a mixture and adjusting the pH of said mixture to about 9 – 12.

Another method for preparing certain compositions of the invention includes the steps of preparing a non-colloidal size magnetic particle dispersion by adding the particles to a mixture of a viscosity additive in a carrying fluid,  
20 preparing a colloidal size magnetic particle dispersion with a stabilizer in a carrying fluid, preparing a colloidal size polishing particle dispersion in a carrying fluid, mixing said colloidal size magnetic particle dispersion and said colloidal size polishing particle dispersion to form an intermediate mixture, mixing the intermediate mixture with the non-colloidal size magnetic particle dispersion,  
25 and adjusting the pH of the composition to a pH in the range from about 9 to about 12.

The invention also teaches several specific compositions one of which includes: colloidal size magnetic particles comprised of colloidal size magnetite ( $\text{Fe}_3\text{O}_4$ ) particles having a weight percent content ranging from about 20 to  
30 about 55 wt % of said composition, colloidal size polishing particles comprised of colloidal size silica ( $\text{SiO}_2$ ) particles having a weight percent content ranging from about 1 to about 20 wt. % of said composition, at least one stabilizer

comprised of tetramethylammonium hydroxide having a weight percent content ranging from about 0.05 to about 25 wt. % of said composition. and a carrier fluid, adjusted to a pH in excess of 9, comprising any remaining wt % of said composition.

5        Another composition taught includes: non-colloidal size magnetic particles selected from carbonyl iron or magnetite particles, the particles having a weight percent content from about 21 to about 38.5 wt %. The composition also includes colloidal size magnetic particles comprising colloidal size magnetite particles having a weight percent content from about 3 to about 7.5 wt  
10   % and colloidal size polishing particles comprised of colloidal size silica particles having a weight percent content from about 1 to about 10 wt %. It also includes a stabilizer, tetramethylammonium hydroxide having a weight percent content from about 0.5 to about 10 wt. % and a viscosity adjusting additive comprising polyethylene glycol having a weight percent content from about 0.1 to about 5  
15   wt. %. Finally, the composition is completed with a carrier fluid adjusted to a pH in excess of 9. The carrier fluid comprises the remaining wt % of the composition.

      A third composition taught by the present invention includes magnetic particles which are carbonyl iron particles. These iron particles have a weight  
20   percent content in the composition from about 20 to about 55 wt. %. The composition also includes colloidal size polishing particles comprised of colloidal size silica particles having a weight percent content in said composition from about 1 to about 20 wt. % and at least one stabilizer comprised of tetramethylammonium hydroxide having a weight percent content in said  
25   composition ranging from about 0.5 to about 25 wt. %. The composition also has an additive for adjusting viscosity, specifically polyethylene glycol, which has a weight percent content in the composition ranging from about from about 0.1 to about 10 wt. %. Finally, a carrier fluid, adjusted to a pH in excess of 9, comprises the remaining wt % of the composition..

30        Yet another embodiment of the present invention teaches a magnetic polishing fluid composition comprising colloidal size magnetic particles with a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ , colloidal size

polishing particles with a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ , at least one stabilizer for stabilizing said colloidal size particles, at least one oxidizer, at least one inhibitor for controlling the rate of oxidation of the oxidizer, and a carrying fluid where the pH of the composition is in the range  
5 from between about 0.5 to about 5.5.

In another embodiment based on the above, the magnetic polishing fluid composition does not include colloidal polishing particles. In yet another embodiment based on the above, the polishing fluid does not contain an inhibitor.

10 A method for preparing the above compositions includes the steps of preparing a colloidal size magnetic particle dispersion with a stabilizer in a carrying fluid, preparing a colloidal size polishing particle dispersion in a carrying fluid, adding to the colloidal size polishing particle dispersion at least one oxidizer and at least one inhibitor, mixing said colloidal size magnetic particle  
15 dispersion and said colloidal size polishing particle dispersion to form a mixture, and adjusting the mixture to a final pH of about 0.5-5.5, if not already at that pH.

In yet another embodiment, a multi-phase magnetic composition, a magnetic polishing fluid composition contains both colloidal and non-colloidal  
20 magnetic particles. The non- colloidal magnetic particles have a mean particle size range from about 0.15  $\mu\text{m}$  to about 3.0  $\mu\text{m}$  and the colloidal magnetic particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ . The composition also contains at least one oxidizer, at least one inhibitor for inhibiting the rate of oxidation of said oxidizer, at least one stabilizer for  
25 stabilizing said colloidal particles, an additive for adjusting viscosity, and a carrying fluid. The pH of the final composition is in a range from about 0.5 to about 5.5.

Yet another multi-phase embodiment, does not include an inhibitor while a second multiphase embodiment does not require colloidal polishing particles.

30 The invention also teaches a method for producing the above composition comprising the steps of preparing non-colloidal size magnetic particle dispersion by adding the particles to a mixture of a viscosity additive in a



carrying fluid. Preparation of a colloidal size magnetic particle dispersion with a stabilizer in a carrying fluid follows. This is further followed by preparing a colloidal size polishing particle dispersion in a carrying fluid and adding to the colloidal size polishing particle dispersion at least one oxidizer and at least one inhibitor. The colloidal size magnetic particle dispersion and the colloidal size polishing particle dispersion are mixed to form an intermediate mixture, which is then mixed with the non-colloidal size magnetic particle dispersion. Finally, the pH of the composition is adjusted to a pH in the range of about 0.5 to about 5.5, if the composition is not already at the proper pH in that range.

In yet another embodiment, a magnetic polishing fluid composition is taught which comprises magnetic particles having a mean particle size range from about 0.15 to about 3.0  $\mu\text{m}$ , colloidal size polishing particles having a mean particle size range from about 0.01 to about 0.1  $\mu\text{m}$ , at least one oxidizer, at least one inhibitor for inhibiting the rate of oxidation by the oxidizer, at least one stabilizer for stabilizing the colloidal particles, an additive for adjusting viscosity, and a carrying fluid, where the pH of the composition is from about 0.5 to about 5.5

Various specific compositions are taught by the present invention. One such composition includes colloidal size magnetic particles comprise colloidal size magnetite ( $\text{Fe}_3\text{O}_4$ ) particles. These particles have a weight percent content of the total composition ranging from about 20 to about 55 wt %. Colloidal size polishing particles comprising colloidal size alumina ( $\text{Al}_2\text{O}_3$ ) particles having a weight percent content in the total composition ranging from about 1 to about 20 wt % is another ingredient. Other components include an oxidizer comprising  $\text{Fe}(\text{NO}_3)_3$  having a weight percent content in said composition ranging from about 1 to about 10 wt.%, an inhibitor comprising  $\text{K}_2\text{Cr}_2\text{O}_7$  having a weight percent content in said composition ranging from about 0.01 to about 2 wt.%, a stabilizer comprising perchloric acid having a weight percent content in the composition ranging from about 0.5 to about 20 wt.%, and a carrier fluid adjusted to a pH in the range of about 0.5 to about 5.5 comprising any remaining wt % of said composition.

Another composition taught by the invention includes non-colloidal size magnetic particles selected from carbonyl iron or magnetite particles. These particles have a weight percent content in the final composition of from about 21 to about 38.5 wt %. Colloidal size magnetic particles comprising colloidal size magnetite particles having a weight percent content in said composition from about 3 to about 7.5 wt %, and colloidal size polishing particles comprising colloidal size alumina particles having a weight percent content in said composition from about 1 to about 10 wt % are two other components of the system. A stabilizer comprising perchloric acid having a weight percent content in the composition from about 0.5 to about 10 wt. %, an oxidizer comprising ferric nitrate having a weight percent content in said composition ranging from about 1 to about 10 wt %, an inhibitor comprising potassium dichromate having a weight percent content in the composition ranging from about 0.01 to about 2 wt %, a viscosity adjusting additive comprising polyethylene glycol having a weight percent content in said composition from about 0.1 to about 5 wt. %, and a carrier fluid, adjusted to a pH in the range from about 0.5 to about 5.5, comprising any remaining wt % of said composition.

A third composition taught includes non-colloidal magnetite particles having a weight percent content in the final composition from about 20 to about 55 wt. %, colloidal size polishing particles comprise colloidal size alumina particles having a weight percent content in said composition from about 1 to about 20 wt. %, a stabilizer comprising perchloric acid having a weight percent content in the composition ranging from about 0.5 to about 20 wt. %, a viscosity additive comprising polyethylene glycol having a weight percent content in the composition ranging from about 0.1 to about 10 wt. %, an oxidizer comprising ferric nitrate having a weight percent content ranging from about 1 to about 10 wt. %, an inhibitor comprising potassium dichromate having a weight percent content ranging from about 0.01 to about 2 wt. %, and a carrier fluid, adjusted to a pH in the range from about 0.5 to about 5.5, comprising any remaining wt % of said composition.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the composition of various magnetic polishing fluids (MPFs) which can be used to polish different ceramic metalloid and optical substrates, such as silica, alumina, cerium oxide, silicon and glass. It is particularly advantageous as a composition for polishing silica ( $\text{SiO}_2$ ). By varying the composition of these MPFs, the rate and quality of polishing can be controlled. The MPFs of the present invention polish at lower viscosities than the MRFs cited above, thereby also producing better quality surfaces. It is believed that the magnetic particle polishing process of this invention is abetted by chemical processes similar to those which occur in chemical-mechanical polishing.

The present invention also relates to various magnetic polishing fluid (MPF) compositions that can be used to polish metal substrates and even some ceramic-like materials. Among the metals that can be polished are copper, aluminum, tungsten, titanium, and tantalum, and among the ceramics which can be polished are TiN and TaN. The compositions are particularly advantageous as MPFs for polishing copper interconnects in the semiconductor industry. They can also polish the dielectric layers often present in semiconductor multi-layers.

When polishing metals with the MPFs of the present invention, an oxidizer is used to create a metal oxide on the surface of a metal. In general metal oxides are softer and therefore more easily polished than pure metals. The rate of polishing depends on the concentration of oxidizer present. Usually, an inhibitor is added to control the rate of polishing by slowing the rate of oxidation of the metal surface

A magnetic polishing fluid (MPF) in a magnetic field, although forming a plasticized mass when the field is activated, retains or reverts to the properties of a liquid during the polishing process. When in its plasticized state the mass possesses Bingham properties.

A magnetic polishing fluid comprised of magnetic particles responds to a magnetic field gradient by increasing its viscosity and changing into a plasticized mass. Any polishing particles contained in the fluid are trapped in the plasticized mass and pushed out of the fluid in a direction perpendicular to the gradient.

This mass is an effective polishing tool when it comes into contact with a moving work surface. Upon contacting the polishing surface, and under the shear stress of the abrasion process, the plasticized mass reverts back to an almost liquid state.

5 In addition, when a polishing solution contains magnetic particles, particularly magnetic particles of non-colloidal size, the particles interact and form dendritic structures when plasticized under the influence of magnetic fields. These plasticized structures contain pores. A liquid media containing a polishing slurry comprising colloidal abrasive particles can fill the pores in the plasticized  
10 structure. The polishing rate is enhanced when the pores in the plasticized polishing mass are filled in this manner. The liquid containing the abrasive particles rises to the surface of the plasticized mass through capillary action. At the surface, the polishing particles are pressed by the polishing machine against the work surface.

15 The magnetic polishing fluid compositions of the present invention comprise, at a minimum, at least one type of magnetic particles, colloidal size abrasive particles, a stabilizer, and a carrying fluid. In one embodiment, the magnetic particles are of colloidal size and first dispersed in a stabilizer in a carrying fluid before mixing with colloidal abrasive particles. In another  
20 embodiment, two sizes of magnetic particles are used, one colloidal and one non-colloidal. Each size of magnetic particle is dispersed separately in its own carrying fluid before the two dispersions are mixed. When metals are polished, an oxidizer and usually an inhibitor are added.

For purposes of the present invention, colloidal size magnetic particles  
25 are deemed to be particles with a mean particle size of about 0.15  $\mu\text{m}$  or less, while colloidal size polishing particles are deemed to be particles with a mean particle size of about 0.1  $\mu\text{m}$  or less. For purposes of the present invention, a ceramic is any non-biological material which has neither clearly defined metallic nor non-metallic characteristics and properties. It includes, among other things,  
30 classical ceramics, glasses, and metalloids. It includes many oxide, nitride, boride, and phosphide compounds. Many of the materials used in the optical,

microelectronic and semiconductor industries would be included in the definition of ceramics as used herein.

Certain embodiments of the invention may require a viscosity additive to control viscosity and/or a pH additive to adjust pH. Additives to increase the rate and enhance the quality of the polishing process can be added to the composition, as needed. In all the embodiments discussed, there is little agglomeration or sedimentation in the fluid over a period of one year at room temperature. With MPFs used for metal polishing, the oxidizer should usually be kept separate from the rest of the MPF when stored for long periods of time.

The magnetic particles used in these compositions can be chosen from many different ferrous and non-ferrous magnetic materials. These include, but are not limited to, ferromagnetic metals such as Fe, Ni, and Co, their alloys, ferrites, chromium oxides such as  $\text{CrO}_2$ , iron oxides such as  $\text{Fe}_3\text{O}_4$ , and cobalt oxides such as  $\text{Co}_3\text{O}_4$ . Carbonyl iron or magnetite ( $\text{Fe}_3\text{O}_4$ ), particularly the latter, are the preferred sources for non-colloidal size magnetic particles. The preferred mean particle size range for non-colloidal magnetic particles is generally about 0.15-3.0  $\mu\text{m}$ , and even more preferably 0.5-1.0  $\mu\text{m}$ .

Capillary action is needed to transport the liquid containing the abrasive colloidal particles to the surface of the plasticized magnetic particle mass. The magnetic particles form quasi-columns with the pathways between them thought of as capillary tubes. The average diameter of the capillary is determined by magnetic particle size. The capillary must be narrow enough to generate a large capillary force but not too narrow to be clogged by abrasive particles. A rough calculation based on these principles, assuming abrasive particles with diameters of about 0.1 micron, can establish 3 microns as an approximate upper bound for the magnetic particles that should be used.

Colloidal magnetite ( $\text{Fe}_3\text{O}_4$ ), the preparation of which is described below, is the preferred source of colloidal magnetic particles. The particles are formed from a mixed ferrous-ferric chloride solution to which either ammonium hydroxide, NaOH or urea is added. Methods for preparing colloidal magnetite other than the one disclosed herein below can also be used, such as the method of Massarat (IEEE Transactions of Magnetism, Vol. Mag 17 (#2) March

1981). Colloidal magnetic dispersions are also commercially available from manufacturers such as Ferrofluids, Inc. The preferred mean particle size range for colloidal magnetic particles is generally about 0.01-0.15  $\mu\text{m}$ , preferably 0.03-0.05  $\mu\text{m}$ .

5 Colloidal size polishing particles can be chosen from many types of oxides, such as  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{ThO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{CeO}_2$ ,  $\text{SiO}_2$  or  $\text{ZnO}$ . Colloidal size particles of carbides e.g.  $\text{SiC}$ , nitrides e.g.  $\text{Si}_3\text{N}_4$  and polycrystalline diamond can also be used as abrasives. The colloidal polishing particles, preferably silica ( $\text{SiO}_2$ ), generally have a mean particle size range of about 0.01-0.1  $\mu\text{m}$ . An  
10 even more preferred mean particle size range for the polishing particles is 0.03-0.05  $\mu\text{m}$ . In the case of diamond, nanometer size particles can be used.

A stabilizing additive for the colloidal particles in MPFs used for polishing ceramics can be chosen from many different non-ionic, anionic and cationic stabilizers, particularly from the group of alkylated ammonium hydroxides. When  
15 ceramics are polished, the preferred stabilizing agent is tetramethylammonium hydroxide (TMAH), which also helps adjust pH. Surfactants that can be used as stabilizers are polydispersed nonylphenol, sodium polyethoxylate, sodium dodecylsulfonate, decylmethylsulfoxide and sodium lignosulfonates. The same stabilizer is usually, but not necessarily, used to stabilize both colloidal size  
20 magnetic and colloidal size polishing particles. Use of low molecular weight stabilizers are preferred since high molecular weight stabilizers, and in particular polymeric surfactants, decrease the rate of polishing, sometimes by as much as a factor of four or five.

All of the magnetic polishing fluids require a carrying fluid. The preferred  
25 carrier fluid in all embodiments is water, and even more preferably de-ionized water. Water is a preferred carrying fluid, particularly advantageous when organic residues are problematic, as is often the case in the microelectronic industry.

Other carrying fluids can also be used. These include, but are not limited  
30 to, polar organic solvents, such as alcohols and ketones, and mixtures of water and polar organic solvents.

In some embodiments, especially those using non-colloidal magnetic particles, viscosity additives may be required. These can be chosen from water soluble polar polymeric materials, such as polyalcohols, having molecular weights (MW) of about 300,000 to about 1,000,000. A preferable viscosity  
5 additive is polyethylene glycol (PEG). A typical static viscosity for the MPFs of this invention, that is the viscosity of the composition when not being used for processing, is about 300-1200 cps.

KOH, NaOH, and tetramethylammonium hydroxide, preferably the latter, and acidic compounds such as acetic acid and other weak organic acids can be  
10 used to adjust pH, when polishing ceramics. The pH of the magnetic fluids should be in excess of pH 9, preferably in the range of about 9 to about 12. The exact pH of an MPF composition depends on its intended use. Polishing silica wafers, for example, requires a pH in the 10.5-11 range, while polishing different types of glasses requires pHs of 11.8-12.0.

15 The MPFs for polishing ceramics can be prepared in several ways, the exact method of preparation depending on the composition of the fluid. A preferable method for preparing MPFs of this invention usable for polishing ceramics is a multi-step process.

When non-colloidal size magnetic particles are used, a dispersion of  
20 such particles in a carrying fluid is prepared. The powder is usually dispersed in the presence of a viscosity additive, after the additive has been mixed into the carrier fluid. When the carrier fluid itself is a multi-component system, the carrier fluid is usually prepared from its components prior to adding the viscosity additive.

25 The method for preparing a colloidal magnetic particle dispersion is similar to that of the non-colloidal one discussed immediately above except that a stabilizer replaces the viscosity additive. The colloidal magnetic powder can be purchased or synthesized. When the colloidal powder is synthesized, the stabilizing agent is usually added directly to the powder immediately after  
30 synthesis. Colloidal size iron particles can be synthesized as described in Example II below or by other methods described in the literature.

A dispersion of stabilized colloidal size polishing particles in a carrying fluid is then prepared. The stabilized colloidal dispersion can be prepared by any known method. For example, if  $\text{SiO}_2$  is used as the polishing agent, a colloidal dispersion can be prepared by dialysis, reaction of sodium silicate with acid, or ion exchange. Commercially available colloidal polishing particle  
5 dispersions can also be used.

After the colloidal polishing particle dispersion and either the non-colloidal magnetic particle or the colloidal magnetic particle dispersion have been prepared, the magnetic particle dispersion and the polishing dispersion are  
10 gradually mixed together while stirring vigorously. If necessary, the pH of the mixture is then adjusted to a value in excess of 9, preferably from about 9 to about 12.

The magnetic particle, polishing particle and stabilizer contents in the final MPF compositions used to polish ceramics range from about 20 to about  
15 55 weight percent (wt. %), from about 1 to about 20 wt. %, and from about 0.5 to about 25 wt. %, preferably from about 25 to about 35 wt %, from about 3 to about 15 wt. %, and from about 1 to about 8 wt. %, respectively. When a viscosity additive is required, it is present in the final MPF composition in a wt % range varying from about 0.1 to about 10 wt %, preferably from about 1 to about  
20 5 wt %. Generally, the larger the weight percent of stabilizers used, the slower the rate of polishing. It is to be understood that when the weight percents of the above components do not total 100%, the remainder is made up by the carrier fluid adjusted to the proper pH.

A multi-phase magnetic polishing fluid for polishing ceramics can be  
25 prepared as follows. Separate dispersions of non-colloidal magnetic particles, colloidal magnetic particles and colloidal polishing particles are prepared as described above. After the three dispersions have been prepared, the stabilized colloidal polishing particle dispersion is slowly added to, and mixed vigorously with, the stabilized colloidal magnetic particle dispersion to form an intermediate  
30 dispersion. The intermediate dispersion is gradually mixed with the non-colloidal magnetic particle dispersion, while stirring vigorously. If necessary, the pH of the



final product is then adjusted to a pH in excess of 9, preferably from about 9 to about 12.

The percentages of non-colloidal magnetic, colloidal magnetic and colloidal polishing particles in the final MPF composition are 21-38.5, 3-7.5 and 1-10 wt %, preferably 25-28, 3.75-5.25 and 3-5 wt %, respectively. The proportions of the stabilizer and viscosity additive range from about 0.5 to about 10 wt. % and from about 0.1 to about 5 wt. %, preferably from about 0.5 to about 5 wt % and from about 1 to about 5 wt. %, respectively. It is to be understood that when the weight percents of the above components do not total 100%, the remainder is made up by the carrier fluid adjusted to the proper pH. Generally, the ratio of non-colloidal to colloidal magnetic particles should be from about 4.9:1 to about 6.1:1, preferably from about 5.3:1 to about 5.7:1.

In the multi-phase embodiment, a method of preparation was described wherein the colloidal polishing particle dispersion is first mixed with a colloidal magnetic particle dispersion. The resulting intermediate dispersion is then further mixed with the non-colloidal magnetic particle dispersion. An alternate, but equally acceptable, procedure would be to first mix the abrasive and non-colloidal magnetic dispersions to form an intermediate dispersion which in turn would be mixed with the colloidal magnetic dispersion.

MPFs for use in polishing ceramics can contain optional additives for increasing the rate and enhancing the quality of the polishing process. Examples of such additives are ammonium molybdate and zirconium sulfate, where the former serves as a chelating agent for abraded  $\text{Si(OH)}_4$  while the latter serves to increase the polishing rate. Small amounts of cerium hydroxide are often added to improve polishing quality. Zinc salts are optional additives that act as a precipitant for removing attrited silica. When using any of the above additives, they are usually added in amounts ranging from about 0.5 to about 4.5 wt. %. The exact amount depends on the additive being used and the substrate being polished. These additives are generally added to the colloidal polishing particle dispersion immediately after it is prepared.

MPFs for polishing metals (and some ceramic materials, such as TiN and TaN) usually include at least one oxidizer selected from the group consisting of

Fe(NO<sub>3</sub>)<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, KIO<sub>3</sub>, and K<sub>3</sub>[Fe(CN)<sub>6</sub>] with the first two being most preferable. The fluid also usually includes at least one inhibitor selected from the group consisting of toluidine, β-naphthylamine, K<sub>2</sub>CrO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, K<sub>2</sub>MoO<sub>4</sub>, and benzotriazol, preferably at least one of the last three. The oxidizer is needed for  
5 producing a thin oxide film on the metal substrate and the inhibitor is required for passivation of the metal surface, thereby controlling the rate of polishing. The exact choice of additives and inhibitors and their amounts depend on the metal being polished. The oxidizers and inhibitors are usually added directly to the colloidal polishing dispersion immediately after its preparation.

10 Stabilizing additives for MPFs used in metal polishing can be chosen from many different non-ionic, anionic and cationic stabilizers. In a preferred embodiment of the invention the stabilizing agent is perchloric acid (HClO<sub>4</sub>), which also helps adjust pH. Other stabilizers which can be used are Fe(NO<sub>3</sub>)<sub>3</sub>, polyethylene (10) isooctylphenyl, polydispersed nonylphenol, sodium  
15 polyethoxylate, sodium dodecylsulfonate, decylmethylsulfoxide and sodium lignosulfonates. The same stabilizer is usually, but not necessarily, used to stabilize both the colloidal size magnetic and colloidal size polishing particles.

The pH of MPF compositions used to polish metals usually range from about 0.5 to about 5.5, preferably 1.5 – 4.5. The exact pH of a composition  
20 depends on its intended use. Tungsten can be polished with compositions having pHs of about 4.1-4.2, while aluminum requires compositions with pHs of about 1.9-2.0. The pH is adjusted using organic and inorganic acids, such as acetic acid, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl, with the last three being most preferred.

25 The methods and procedures for preparing MPF compositions for polishing metals are the same as those used to prepare compositions to polish ceramics. The only differences between the two types of MPFs are the pH ranges used and usually the presence of at least one oxidizer and at least one inhibitor.

30 The magnetic particle, polishing particle and stabilizer contents in single-phase MPF compositions used for metal polishing range from about 20 to about 55 wt. %, from about 1 to about 20 wt. %, and from about 0.5 to about 20

wt. %, preferably from about 25 to about 35%, from about 3 to about 15 %, and from about 1 to about 8 wt. %, respectively. When a viscosity additive is required, it is present in the final MPF composition in a wt % range varying from about 0.1 to about 10 wt %, preferably from about 1 to about 5 wt %. The concentrations of the oxidizer and inhibitor range from about 1 to about 10 wt % and from about 0.01 to about 2 wt %, preferably from about 2 to about 7 wt % and from about 0.03 to about 0.9 wt % %, respectively. It is to be understood that when the weight percents of the above components do not total 100%, the remainder is made up by the carrier fluid adjusted to the proper pH.

The proportions of non-colloidal magnetic, colloidal magnetic and colloidal polishing particles in multi-phase MPF compositions suitable for use in polishing metals are 21-38.5, 3-7.5 and 1-10 wt %, preferably 25-28, 3.75-5.25 and 3-5 wt %, respectively. The proportions of the stabilizer and viscosity additive range from about 0.5 to 10 wt. % and from about 0.1 to 5 wt. %, preferably from about 0.5 to 5 wt % and from about 1 to 5 wt. %, respectively. The concentrations of the oxidizer and inhibitor range from about 1 to 10 wt % and from about 0.01 to 1 wt%, preferably from about 2 to 7 wt % and from about 0.03 to 1.2 wt. %, respectively. It is to be understood that when the weight percents of the above components do not total 100%, the remainder is made up by the carrier fluid adjusted to the proper pH as discussed above. As with multi-phase MPFs used to polish ceramics, the ratio of non-colloidal to colloidal magnetic particles, in general, should be about 4.9:1 to about 6.1:1, preferably from about 5.3:1 to about 5.7:1.

In previously described embodiments of MPF compositions used for metal polishing, the oxidizers are added during the preparation of the polishing fluid. In other embodiments, the oxidizer can be added to the other, already mixed, components, immediately prior to the composition's use. This extends the shelf-life of the MPF.

In previously described embodiments of MPFs for metal polishing, a colloidal polishing solution is always part of the MPF. However, other MPF embodiments produce satisfactory polishing results without containing a colloidal polishing agent.

In previously described metal polishing embodiments, an inhibitor is always present. It has been found that reasonable polishing results may be obtained on occasion, and under certain conditions, without the inclusion of an inhibitor in the MPF.

5 The polishing fluids of the present invention can be used with many of the magnetic polishing machines discussed in the literature. Typical magnetic polishing machines are described in US Patent Nos. 4,821,466, 5,449,313, 5,577,948, 5,616,066, and 5,839,944. In addition, the compositions of the present invention were tested using a polishing machine that employs a series  
10 of intermittent impacts from a plasticized quasi-solid MPF.

The high pH MPF compositions of the present invention can be used to polish ceramic wafers for the microelectronics industry, optical materials, superconductor lamina, ceramic aircraft bearings, and materials for micro-electromechanical systems (MEMS). The acidic polishing compositions  
15 described above, usually containing at least one oxidizer and at least one inhibitor, can be used to polish metal interconnects, dielectric layers in semiconductors, plugs and layers for the microelectronics industry, metallic tubing, and other metal surfaces.

The following are several magnetic polishing fluid compositions suitable for polishing ceramics prepared using the procedures described above.  
20

#### Example I

A dispersion of magnetic particles in a carrying fluid was prepared by mixing 35 g of carbonyl iron (Sigma, particle size 3  $\mu\text{m}$ ) and 65 g of a 30% solution of polyethylene glycol (molecular weight 20000) in de-ionized (DI)  
25 water. The PEG/water mixture was prepared before the carbonyl iron was added. 10 g of a 50 wt. % colloidal silica dispersion (Nalco Ltd., particle size 0.02 - 0.05  $\mu\text{m}$ ) was gradually added to 90 g of the magnetic particle dispersion. The content of the magnetic and colloidal  $\text{SiO}_2$  particles in the final product was 31.5 and 5 wt %, respectively.

30

### Example II

Colloidal magnetite ( $\text{Fe}_3\text{O}_4$ ) was synthesized according to the following procedure. Aqueous solutions of Fe (III) chloride and Fe (II) chloride, each 10 wt % in their respective iron chloride, were mixed. The final molar ratio in the mixture was 2:1  $\text{FeCl}_3$  :  $\text{FeCl}_2$ . A 25 % aqueous solution of  $\text{NH}_4\text{OH}$  was added to the mixture so that the molar ratio of Fe (II) /  $\text{NH}_3$  was 19:1 in the mixture.

The solution was carefully stirred to hydrolyze the iron salts, forming a colloidal magnetite ( $\text{Fe}_3\text{O}_4$ ) dispersion (particle size 0.01 – 0.02  $\mu\text{m}$ ). A stabilizing agent, tetramethylammonium hydroxide, in an amount of 10 wt % with respect to the magnetic powder was added to the colloidal magnetite dispersion immediately after the  $\text{Fe}_3\text{O}_4$  was formed. The stabilized dispersion was concentrated by vacuum filtration to a magnetite content of 29 wt. %.

A colloidal silica dispersion containing 50 wt. %  $\text{SiO}_2$ , (Nalco Ltd., particle size 0.02 – 0.05  $\mu\text{m}$ ) was gradually added to the colloidal magnetic dispersion with vigorous stirring. The amount of colloidal silica added produced a final product with a  $\text{SiO}_2$  content of 5 wt. %. The final product was a fluid comprising 26 wt. % of colloidal magnetic powder and 12.6 wt % tetramethylammonium hydroxide and had a pH of 10.

The magnetic polishing fluid that was obtained exhibited a magnetization saturation of 550 Gs and a viscosity of 500 cps.

### Example III

A carrying fluid for the dispersion of non-colloidal magnetic particles was prepared by dissolving 30 g of polyethylene glycol (molecular weight 20000) in 70 g of de-ionized (DI) water. A dispersion of non-colloidal magnetic particles was prepared by mixing 90 g of non-colloidal magnetite ( $\text{Fe}_3\text{O}_4$ ) powder (Aldrich, particle size 5  $\mu\text{m}$ ), with 10 g of the polyethylene glycol/water solution. To produce a finer particle, the dispersion was triturated for one hour with an Attritor model 01-HDDM. The powder produced had a particle size of less than 1  $\mu\text{m}$  but greater than 0.5  $\mu\text{m}$ .

Colloidal magnetic particles of magnetite ( $\text{Fe}_3\text{O}_4$ ) were synthesized using the method described in Example II. A dispersion of the stabilized colloidal

magnetic particles was prepared also as described in Example II. The dispersion containing the stabilizer was concentrated by vacuum filtration to a magnetite content of 37 wt. %.

16.32 g of a 50 wt. % colloidal silica dispersion (Nalco Ltd., particle size 0.02  $\mu\text{m}$ ), was gradually added to 44.88 g of the colloidal magnetic particle dispersion while stirring vigorously. The content of the colloidal magnetic particles and the colloidal  $\text{SiO}_2$  particles in the dispersion mixture was 8.6 % and 13.8 wt. %, respectively. The product obtained had a pH of 10.0.

38.8 g of the non-colloidal magnetic particle dispersion were gradually mixed with 61.2 g of the dispersion containing the colloidal  $\text{Fe}_3\text{O}_4$  and  $\text{SiO}_2$  particles. Mixing was accompanied by continuous vigorous stirring. The content of the non-colloidal magnetic particles, colloidal magnetic particles and colloidal silica particles in the final product was 35.0, 5.0, 8.5 wt. %, respectively.

#### Example IV

A dispersion of colloidal magnetic particles was prepared as in Example III and concentrated by vacuum filtration to a magnetite content of 30 %.

23 g of a 50 wt. % colloidal  $\text{SiO}_2$  dispersion (Nalco Ltd., particle size 0.02  $\mu\text{m}$ ), was added gradually to 50 g of the colloidal magnetic particle dispersion prepared previously. The two dispersions were mixed while stirring vigorously. In the mixture, the colloidal magnetic particles and colloidal polishing particles had particle contents of 30 and 5 wt. % respectively. Using KOH, the mixed dispersion was adjusted to a pH of 10.4. When 0.6 wt. % of zirconium sulfate was added to the dispersion, its  $\text{SiO}_2$  wafer polishing rate increased from 450  $\text{\AA}/\text{min}$  to 1200  $\text{\AA}/\text{min}$  without adversely affecting roughness.

#### Example V

A carrying fluid for the dispersion of non-colloidal magnetic particles was prepared by dissolving 1g of polyethylene glycol (molecular weight 20000) in 99 g of de-ionized water. A dispersion of non-colloidal magnetic particles was prepared by mixing 90 g of non-colloidal magnetite ( $\text{Fe}_3\text{O}_4$ ) powder (Aldrich, particle size 3  $\mu\text{m}$ ), with 10 g of the polyethylene glycol solution. To produce a

finer particle, the dispersion was trituated for one hour with an Attritor model 01-HDDM. The powder produced had a particle size of less than 1  $\mu\text{m}$  but greater than 0.5  $\mu\text{m}$ .

Colloidal magnetic particles of magnetite ( $\text{Fe}_3\text{O}_4$ ) were synthesized using the method described in Example II. A dispersion of the stabilized colloidal magnetic particles was prepared also as described in Example II. The stabilizer used with the colloidal magnetic particles was sodium lignosulfonate and the dispersion was 10 wt. % in magnetic powder. The sodium lignosulfonate was added to the colloidal particles immediately after their formation. The stabilized colloidal magnetic dispersion was concentrated by vacuum filtration to a magnetite content of 37 wt. %.

50 g of a 50 wt. % colloidal silica dispersion (Nalco Ltd., particle size 0.02  $\mu\text{m}$ ), was gradually added to 50 g of the colloidal magnetic particle dispersion while stirring vigorously. The content of the colloidal magnetic particles and the colloidal  $\text{SiO}_2$  particles in the dispersion mixture was 17.8 % and 25.0 wt. %, respectively. The product obtained had a pH of 10.0.

60 g of the non-colloidal magnetic particle dispersion were gradually mixed with 40 g of the dispersion containing the colloidal  $\text{Fe}_3\text{O}_4$  and  $\text{SiO}_2$  particles. Mixing was accompanied by continuous vigorous stirring. The content of the non-colloidal magnetic particles, colloidal magnetic particles and colloidal silica particles in the final product was 37.0, 5.1, 7.5 wt. %, respectively. The pH of the final polishing composition was 10 after being adjusted with a 50 wt % KOH solution.

Table I below shows the polishing results obtained when several of the examples prepared above were used as polishing fluids.

Table I

Example No.	Polished Material	Removal Rate, Å/min	Average Roughness, Å	Within Wafer Non-Uniformity (WIWNU), %
I	PECVD TEOS SiO <sub>2</sub>	3500	4.22	---
II	PECVD TEOS SiO <sub>2</sub>	700	0.99	0.2
III	PECVD TEOS SiO <sub>2</sub>	3000	1.63	0.5
V	PECVD TEOS SiO <sub>2</sub>	3500	3.68	---
MRF	PECVD TEOS SiO <sub>2</sub>	2500	7.38	---

PECVD TEOS SiO<sub>2</sub> is an acronym for plasma enhanced chemical vapor deposition, tetraethylorthosilicate silica.

The sample indicated as MRF was prepared by a typical prior art method described in US Patent No. 5577948, column 9, Example 1.

The removal rate of the silicon wafers was measured using a Nanospec instrument located at the Israel Institute of Technology, Microelectronic Center, Haifa Israel. Surface roughness was measured using an atomic force microscope located at the Wolfson Applied Materials Research Center of Tel Aviv University.

The optimal ratio of non-colloidal to colloidal magnetic particles in multi-phase MPFs was experimentally determined. A series of plasma enhanced chemical vapor deposition PECVD TEOS silica wafers was polished using a multi-phase MPF with a constant 25 wt. % non-colloidal magnetic particle content. The wt % of the colloidal magnetic particles in the MPF was varied. The following were the results of the experiments:



Table II

Non-colloidal: colloidal magnetic particle ratio	WIWNU, %	Removal rate , Å/min
3	6.3	2882
4	6.0	2800
4.5	5.6	2790
5	2.8	2750
5.2	2.6	2740
5.5	2.4	2720
6	2.4	2680
6.1	2.4	2650
6.5	2.4	2200
7	2.5	1800
7.5	2.7	1600

Surprisingly, the results of the experiments show that while removal rate decreases monotonically with additional colloidal size magnetic particles, within wafer non-uniformity (WIWNU) does not. There appears to be a broad but definite minimum in the WIWNU figure of merit. The optimal range for the non-colloidal/ colloidal particle ratio in a multi-phase system appears to be somewhere between about 4.9:1 and about 6.1:1, preferably between about 5.3:1 and about 5.7:1.

Experiments were carried out to determine the pH dependency on polishing quality using the MPFs of this invention. A PECVD TEOS silica wafer was polished using SiO<sub>2</sub> abrasives. The results in Table III show a rapid increase in removal rate at high pHs.

Table III

PH	2	4	6	8	10	11	12
Removal rate, Å	150	200	1000	1200	3720	3800	3690

Experiments were carried out to see the effect of abrasive particle size on polishing quality using the various magnetic particle embodiments of this invention. Conditions were kept constant for all three experiments, except as noted. The results are summarized in Table IV.

Magnetic polishing of ceramic surfaces using the MPFs of the present invention which contain colloidal magnetic particles provide a better quality polished surface than MPFs containing both non-colloidal and colloidal magnetic particles. However, the polishing rate of the former is slower, 50-100 nm/min. A colloidal MPF can be used for fine polishing, where surface roughnesses of  $< 1$  Å are required. The finer polishing can be carried out in the later stages of a multi-stage polishing process.

Table IV

Abrasive Particle Size, microns	Surface Roughness, Å Non-colloidal Magnetic Particle MPF	Surface Roughness, Å Colloidal Magnetic Particle, MPF	Surface Roughness, Å Multi-phase Magnetic Particle MPF
0.01	1.2	0.9	0.95
0.03	1.58	0.95	1.22
0.04	1.9	1.0	1.30
0.05	2.1	1.04	1.34
0.07	3.6	1.10	2.1
0.09	4.2	1.12	2.36
0.1	4.8	1.13	2.48
0.2	5.4	1.6	4.44
0.3	8.6	1.8	5.12
0.4	8.0	1.92	5.8
0.5	8.6	2.1	6.4
1.0	9.4	2.8	7.42

An MPF of the present invention that contains only non-colloidal  
 5 magnetic particles provides faster polishing rates, e.g. 350 nm/min, than an  
 MPF containing both colloidal and non-colloidal magnetic particles. The quality  
 of the surface, however, will be inferior with a roughness of ~ 5 Å. An MPF  
 containing both colloidal and non-colloidal particles can be used for relatively  
 coarse polishing, particularly during the initial stages of a multi-stage polishing  
 10 process.

The following are several magnetic polishing fluid compositions suitable  
 for polishing metals prepared using the procedures described above.

## Example VI

A carrying fluid for preparing a dispersion of non-colloidal magnetic particles was formed by dissolving of 1g polyethylene glycol (1000000 g/mol) in 99 g of de-ionized water. A dispersion of non-colloidal magnetic particles was prepared by mixing 90 g magnetite ( $\text{Fe}_3\text{O}_4$ ) powder with 10 g of the polyethylene glycol/water carrying fluid. Powdered  $\text{Fe}_3\text{O}_4$  (Aldrich, particle size 3  $\mu\text{m}$ ) was triturated in a laboratory grinder for an hour until the powder had a particle size of between about 0.5 and 1  $\mu\text{m}$ .

Colloidal magnetite ( $\text{Fe}_3\text{O}_4$ ) was synthesized according to the following procedure. Aqueous solutions of Fe (III) chloride and Fe (II) chloride, each 10 wt % in their respective iron chloride, were mixed. The final molar ratio in the mixture was 2:1  $\text{FeCl}_3$  :  $\text{FeCl}_2$ . A 25 % aqueous solution of  $\text{NH}_4\text{OH}$  was added to the mixture so that the molar ratio of Fe (II) /  $\text{NH}_3$  was 19:1 in the mixture.

The solution was carefully stirred to hydrolyze the iron salts, forming a colloidal magnetite ( $\text{Fe}_3\text{O}_4$ ) dispersion (particle size 0.01 – 0.02  $\mu\text{m}$ ). A stabilizing agent, 2 M perchloric acid, in an amount of 10 wt % with respect to the magnetic powder was added to the colloidal magnetite dispersion immediately after the  $\text{Fe}_3\text{O}_4$  was formed. The stabilized dispersion was concentrated by vacuum filtration to a magnetite content of 30 wt. %.

50 g of a dispersion, containing 50 wt. %  $\text{Al}_2\text{O}_3$ , (Metron, particle size 0.02  $\mu\text{m}$ ) was gradually added to 50 g of the colloidal magnetic particle dispersion while stirring vigorously. The colloidal magnetic particle and colloidal  $\text{Al}_2\text{O}_3$  particle content in the final dispersion were 17.8 and 25 wt. %, respectively. The final product was a homogeneous fluid with a pH of 2.7. At this point, 13.4 g of  $\text{Fe}(\text{NO}_3)_3$  and 2.1 g of  $\text{K}_2\text{CrO}_4$  were added to the polishing particle dispersion.

50 g of the non-colloidal magnetic particle dispersion were gradually added to 50 g of the dispersion containing the colloidal  $\text{Fe}_3\text{O}_4$  and  $\text{Al}_2\text{O}_3$  particles. During the addition process, the mixture was vigorously stirred. The non-colloidal magnetic particle, colloidal magnetic particle, and colloidal abrasive particle content in the final product was 45, 8.9, 12.5 wt. %, respectively. Nitric acid was added to adjust the pH of the final product to 1.9

The oxidizer ( $\text{Fe}(\text{NO}_3)_3$ ) and the inhibitor ( $\text{K}_2\text{CrO}_4$ ) concentrations in the final product were 7 wt. % and 0.9 wt. %, respectively.

#### Example VII

- 5 A non-colloidal / colloidal magnetic / abrasive particle multi-phase MPF was prepared as in Example I. Benzotriazol was also added as an inhibitor to the polishing particle dispersion prepared in Example I. The final pH was adjusted with KOH and acetic acid to a value of 4.1. The final concentrations of  $\text{H}_2\text{O}_2$ ,  $\text{K}_2\text{CrO}_4$  and benzotriazol were 7 wt.%, 2.5%, and 0.5%, respectively.
- 10 The results of polishing metal surfaces with the MPFs produced in Examples VI and VII are shown in Table V below.

Table V

Example No.	Polished Material	Removal Rate, Å/min	Roughness, Å	WIWNU, %
VI	Al	1800-2800	4.48	7
VII	Cu	2000-3000	6.22	2.5

- 15 When examined, the polished metal substrates of Table V showed a "peak to valley" value of less than 100 Å, few scratches and no dishing. As seen from the Table, roughnesses of between ~5-10 Å and polishing rates of ~ 250 nm/min were attainable.

- 20 Removal rate was determined by measuring sheet resistance using a conventional four point probe and surface roughness was measured using an atomic force microscope located at the Wolfson Applied Materials Research Center of Tel Aviv University.

#### Example VIII

- 25 Two multiphase MPF compositions were prepared. Both had a ratio of non-colloidal to colloidal magnetic particles of 5.75:1, and both contained 4.5%  $\text{Al}_2\text{O}_3$  and 2.5 wt. % of hydrogen peroxide. One composition also contained 0.5

wt. % potassium dichromate as an inhibitor. Both compositions had their pH adjusted to 1.9 with nitric acid.

The silicon wafer was covered with a layer of TiN and then a layer of Ti. Each layer had a thickness of  $\sim 500$  Å. The multi-layer was capped by an  $\sim$  7000 Å layer of aluminum. Within 120 seconds of the start of polishing, all the surface coatings were ground away and the underlying silicon substrate was reached. The removal rate was calculated as  $\sim 450$  nm/ min. The roughness of the silicon wafer after removal of the layers was  $\sim 8.8$  Å.

#### 10 Example IX

The same MPF as in Example VIII was used on a wafer similar to the one in that Example. Dishing, i.e. the extent of concavity, as determined by a SEM on three different sites on the wafer was found to be less than 150 Å.

#### 15 Example X

A sputtered  $\sim 500$  Å film of TiN was laid down on a silicon wafer. The wafer was then coated by an  $\sim 8000$  Å thick layer of CVD deposited tungsten. The wafer was polished using an MPF similar to that of Example I but with a ferric nitrate concentration of 7%. Another wafer was polished using an MPF similar to that of Example I but using 7 wt % hydrogen peroxide as an oxidizer rather than ferric nitrate. Both MPFs had their pH adjusted to 1.8 using nitric acid. The removal rate for the peroxide MPF was calculated as 2400 Å/min; the ferric nitrate MPF had a removal rate of 3900 Å/min. Roughness of the wafer surface was 40.2 Å and 9.28 Å for the hydrogen peroxide and ferric nitrate MPFs respectively.

#### Example XI

A patterned test wafer having tungsten interconnects was polished using the ferric nitrate MPF of Example X. Dishing, as measured by a SEM, showed that when the tungsten interconnect was narrower than three microns, dishing was negligible. When the line was wider than 100 microns, dishing was less than 300 Å.

### Example XII

A silicon wafer coated with a 500 Å barrier layer of TiN was further coated with a 5000 Å of copper. Three MPFs were used to polish the wafers, a non-colloidal magnetic particle MPF, a colloidal magnetic particle MPF and a multi-phase MPF. All three MPFs contained 2 wt % potassium ferricyanide as an oxidizer. All had their pH fixed at 2.1 by adding nitric acid and acetic acid, with the latter also serving as a buffer. The results are shown in Table VI below.

Table VI

MPF	Removal Rate, Å/min	Roughness, Å	WIWNU %
Colloidal	650	<2.0	3.78
Non-colloidal	2400	15.2	5.8
Multi-phase	2310	4.88	4.4

The formulation prepared in Example VI and used to polish aluminum can also be used to polish titanium and titanium nitride, among other substrates.

The formulation of Example VII used to polish copper can also be used to polish tungsten, among other metals.

### Example XIII

Two multiphase MPF compositions were prepared, both with a ratio of non-colloidal to colloidal magnetic particles of 5.75:1 and both containing 2.5 wt. % of hydrogen peroxide. One composition also contained 0.5 wt. % potassium dichromate as an inhibitor. Both compositions had their pH adjusted to 1.9 with nitric acid.

The two compositions were used to polish silicon wafers coated with an approximate 7000 Å layer of aluminum. The composition with the inhibitor polished away the entire metal coating and reached the underlying silicon substrate within 150 seconds of the start of polishing. The composition without

the inhibitor accomplished the same in 130 seconds. The removal rate was calculated as 280 nm/ min and 323 nm/min for the inhibited and uninhibited compositions, respectively. The roughness of the polished silicon wafers after their aluminum layers had been polished away was 24.8 Å and 40.1 Å for the inhibited and uninhibited compositions, respectively.

#### Example XIV

A multiphase MPF without abrasive particles was prepared. The MPF contained 4.5 wt % ferric nitrate and 1 wt. % potassium dichromate. The composition's pH was adjusted with nitric acid to 1.9. A silicon wafer coated with an ~ 7000 Å layer of aluminum was polished using the above composition. Within 450 seconds of the start of polishing, the entire surface coating was ground away and the underlying silicon substrate was reached. The removal rate was calculated as ~ 120 nm/min. The roughness of the wafer after removal of the layer was ~ 10Å.

While preferred embodiments of the present invention have been described so as to enable one of skill in the art to practice the present invention, the preceding description is intended to be exemplary only. It should not be used to limit the scope of the invention, which should be determined by reference to the following claims.



**What is claimed is:**

1. A magnetic polishing fluid composition comprising:
  - colloidal and non-colloidal magnetic particles, wherein said non-colloidal magnetic particles have a mean particle size range from about 0.15  $\mu\text{m}$  to about 3.0  $\mu\text{m}$  and said colloidal magnetic particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ ;
  - colloidal size polishing particles, wherein said polishing particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ ;
  - at least one stabilizer for stabilizing said colloidal size particles;
  - an additive for adjusting viscosity, and
  - a carrying fluid.
2. A composition according to claim 1 further comprising additives for the enhancement of the rate and quality of the polishing process wherein said additives are selected from the group consisting of zirconium sulfate, zinc salts, ammonium molybdate, and cerium hydroxide.
3. A composition according to claim 1 wherein said non-colloidal size magnetic particles have a mean particle size range from about 0.5  $\mu\text{m}$  to about 1.0  $\mu\text{m}$ .
4. A composition according to claim 1 wherein said colloidal size magnetic particles have a mean particle size range from about 0.03  $\mu\text{m}$  to about 0.05  $\mu\text{m}$ .
5. A composition according to claim 1 wherein the ratio of said non-colloidal magnetic particles to said colloidal magnetic particles ranges from about 4.9:1 to about 6.1:1.
6. A composition according to claim 1 wherein the ratio of said non-colloidal magnetic particles to said colloidal magnetic particles ranges from about 5.3:1 to about 5.7:1.
7. A composition according to claim 1 wherein said colloidal size and non-colloidal size magnetic particles are selected from a group of materials consisting of ferromagnetic metals, their alloys, ferrites, carbonyl iron, iron phosphides cobalt oxides, chromium oxides and iron oxides.

8. A composition according to claim 1 wherein said non-colloidal size magnetic particles are selected from a group consisting of magnetite ( $\text{Fe}_3\text{O}_4$ ) and carbonyl iron particles.
- 5 9. A composition according to claim 1 wherein said colloidal size magnetic particles are magnetite ( $\text{Fe}_3\text{O}_4$ ) particles.
10. A composition according to claim 1 wherein said colloidal size polishing particles have a mean particle size range from about  $0.03\text{ }\mu\text{m}$  to about  $0.05\text{ }\mu\text{m}$ .
- 10 11. A composition according to claim 1 wherein said colloidal size polishing particles are selected from a group consisting of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{ThO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZnO}$ ,  $\text{MgO}$ ,  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$ , polycrystalline diamond,  $\text{SiC}$ , and  $\text{Si}_3\text{N}_4$ .
12. A composition according to claim 1 wherein said colloidal size polishing particles are silica ( $\text{SiO}_2$ ) particles.
- 15 13. A composition according to claim 1 wherein the carrying fluid is water.
14. A composition according to claim 1 wherein said viscosity adjusting additive is a polar polymeric material.
15. A composition according to claim 14 wherein said viscosity adjusting additive is a polyalcohol.
- 20 16. A composition according to claim 15 wherein said viscosity adjusting additive is polyethylene glycol.
17. A composition according to claim 1 wherein said stabilizer is an alkylated ammonium hydroxide.
18. A composition according to claim 17 wherein said stabilizer is tetramethylammonium hydroxide.
- 25 19. A composition according to claim 1 wherein said composition has a pH in excess of about 9.
20. A composition according to claim 1 wherein said composition has a pH in the range from about 9 to about 12.
- 30 21. A magnetic polishing fluid composition according to claim 1 wherein:

said non-colloidal size magnetic particles is selected from a group consisting of carbonyl iron and magnetite particles, said particles having a weight percent content from about 21 to about 38.5 wt %;

5       said colloidal size magnetic particles comprising colloidal size magnetite particles, said particles having a weight percent content from about 3 to about 7.5 wt %;

      said colloidal size polishing particles comprising colloidal size silica particles, said particles having a weight percent content from about 1 to about 10 wt %;

10       said at least one stabilizer comprising tetramethylammonium hydroxide, said hydroxide having a weight percent content from about 0.5 to about 10 wt. %;

      said viscosity adjusting additive comprising polyethylene glycol, said glycol having a weight percent content from about 0.1 to about 5 wt. %;

15       and

      said carrier fluid adjusted to a pH in excess of 9 comprising any remaining wt % of said composition.

22. A composition according to claim 21 further comprising additives selected from among the group of ammonium molybdate, zirconium sulfate, cerium hydroxide and zinc salts in a weight percent ranging from

20       about 0.5 to about 4.5 wt. % of the composition.

23. A composition according to claim 1 wherein said non-colloidal size magnetic particles have a weight percent content in said composition ranging from about 21 to about 38.5 wt. %.

25       24. A composition according to claim 1 wherein said colloidal size magnetic particles have a weight percent content in said composition ranging from about from about 3 to about 7.5 wt. %

25. A composition according to claim 1 wherein said colloidal size polishing particles have a weight percent content in said composition

30       ranging from about 1 to about 10 wt. %.

26. A composition according to claim 1 wherein said at least one stabilizer has a weight percent content in said composition ranging from about 0.5 to about 10 wt. %.
27. A composition according to claim 1 wherein said viscosity additive has  
5 a weight percent content in said composition ranging from about 0.1 to about 5 wt. %.
28. A composition according to claim 1 wherein said non-colloidal size magnetic particles, said colloidal size magnetic particles, said colloidal size polishing particles, said at least one stabilizer and said viscosity  
10 additive have weight percent contents in said composition ranging from about 21 to about 38.5 wt. %, from about 3 to about 7.5 wt. %, from about 1 to about 10 wt. %, from about 0.5 wt. % to about 10 wt. % and from 0.1 to about 5 wt. %, respectively.
29. A composition according to claim 1 wherein said non-colloidal size magnetic particles, said colloidal size magnetic particles, said colloidal size polishing particles, said at least one stabilizer and said viscosity additive have weight percent contents in said composition from about 25  
15 to about 28 wt. %, from about 3.75 to about 5.25 wt. %, from about 3 to about 5 wt. %, from about 0.5 to about 5 wt. % and from about 1 to about 5 wt. %, respectively.
- 20 30. A composition according to claim 1 further comprising at least one oxidizer.
31. A composition according to claim 30 wherein said at least one oxidizer is selected from a group consisting of  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{KIO}_3$ , and  
25  $\text{K}_3[\text{Fe}(\text{CN})_6]$ .
32. A composition according to claim 30 further comprising at least one inhibitor for inhibiting the rate of oxidation of the oxidizer.
33. A composition according to claim 32 wherein said at least one inhibitor is selected from a group consisting of benzotriazol, toluidine,  $\beta$ -naphthylamine,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_2\text{MoO}_4$  and  $\text{K}_2\text{CrO}_4$ .  
30
34. A composition according to claim 30 wherein said colloidal size polishing particles are alumina ( $\text{Al}_2\text{O}_3$ ) particles.

35. A composition according to claim 30 wherein said stabilizer is perchloric acid.
36. A composition according to claim 30 wherein said composition has a pH from about 0.5 to 5.5.
- 5 37. A composition according to claim 30 wherein said composition has a pH from about 1.5 to 4.5.
38. A magnetic polishing fluid composition comprising:
- colloidal and non-colloidal magnetic particles, wherein said non-colloidal magnetic particles have a mean particle size range from about
  - 10 0.15  $\mu\text{m}$  to about 3.0  $\mu\text{m}$  and wherein said colloidal magnetic particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ ;
  - at least one oxidizer;
  - at least one inhibitor for inhibiting the rate of oxidation of said oxidizer;
  - at least one stabilizer for stabilizing said colloidal particles;
  - 15 an additive for adjusting viscosity, and
  - a carrying fluid;
  - wherein the pH of said composition is in a range from about 0.5 to about 5.5.
39. A magnetic polishing fluid composition comprising:
- 20 colloidal and non-colloidal magnetic particles, wherein said non-colloidal magnetic particles have a mean particle size range from about 0.15  $\mu\text{m}$  to about 3.0  $\mu\text{m}$  and wherein said colloidal magnetic particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ ;
  - 25 colloidal size polishing particles, wherein said polishing particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ ;
  - at least one oxidizer;
  - at least one inhibitor for inhibiting the rate of oxidation of said oxidizer;
  - at least one stabilizer for stabilizing said colloidal particles;
  - 30 an additive for adjusting viscosity, and
  - a carrying fluid;

wherein the pH of said composition is in a range from about 0.5 to about 5.5.

40. A composition according to claim 39 wherein:

said non-colloidal size magnetic particles are selected from a group consisting of carbonyl iron and magnetite particles, said particles having a weight percent content in said composition of from about 21 to about 38.5 wt %;

said colloidal size magnetic particles comprising colloidal size magnetite particles, said particles having a weight percent content in said composition from about 3 to about 7.5 wt %;

said colloidal size polishing particles comprising colloidal size alumina particles, said particles having a weight percent content in said composition from about 1 to about 10 wt %;

a stabilizer comprising perchloric acid, said perchloric acid having a weight percent content in said composition from about 0.5 to about 10 wt. %;

an oxidizer comprising ferric nitrate, said ferric nitrate having a weight percent content in said composition ranging from about 1 to about 10 wt %;

an inhibitor comprising potassium dichromate, said potassium dichromate having a weight percent content in said composition ranging from about 0.01 to about 2 wt %;

a viscosity adjusting additive comprising polyethylene glycol, said glycol having a weight percent content in said composition from about 0.1 to about 5 wt. %; and

said carrier fluid, adjusted to a pH in the range from about 0.5 to about 5.5, comprising any remaining wt % of said composition.

41. A composition according to claim 39 wherein said non-colloidal size magnetic particles have a weight percent content in said composition ranging from about 21 wt. % to about 38.5 wt. %.

42. A composition according to claim 39 wherein said colloidal size magnetic particles have a weight percent content in said composition ranging from about 3 wt. % to about 7.5 wt. %.
- 5 43. A composition according to claim 39 wherein said colloidal size polishing particles have a weight percent content in said composition ranging from about 1 wt. % to about 10 wt. %.
44. A composition according to claim 39 wherein said at least one stabilizer has a weight percent content in said composition ranging from about 0.5 wt. % to about 10 wt. %.
- 10 45. A composition according to claim 39 wherein said viscosity additive has a weight percent content in said composition ranging from about 0.1 wt. % to about 5 wt. %.
46. A composition according to claim 39 wherein said at least one oxidizer has a weight percent content in said composition ranging from about 1
- 15 wt. % to about 10 wt. %.
47. A composition according to claim 39 wherein said at least one inhibitor has a weight percent content in said composition ranging from about 0.01 to about 2 wt. %.
48. A composition according to claim 39 wherein said non-colloidal size
- 20 magnetic particles, said colloidal size magnetic particles, said colloidal size polishing particles, said at least one stabilizer, said viscosity additive, said at least one oxidizer and said at least one inhibitor have weight percent contents in said composition ranging from about 21 to about 38.5 wt. %, from about 3 to about 7.5 wt. %, from about 1 to about 10 wt. %, from about 0.5 wt. % to about 10 wt. %, from about 0.1 wt. % to about 5
- 25 wt. %, from about 1 wt. % to about 10 wt. %, and from about 0.01 to about 2 wt. %, respectively.
49. A composition according to claim 39 wherein said non-colloidal size magnetic particles, said colloidal size magnetic particles, said colloidal
- 30 size polishing particles, said at least one stabilizer, said viscosity additive, said at least one oxidizer and said at least one inhibitor have weight percent contents in said composition of from about 25 to about 28 wt. %,

from about 3.75 to about 5.25 wt. %, from about 3 to about 5 wt. %, from about 0.5 to about 5 wt. %, from about 1 to about 5 wt. %, from about 2 to about 7 wt. %, and from about 0.03 to about 1.2 wt.%, respectively.

50. A method for producing a composition according to claim 1, said method comprising the steps of:

preparing a dispersion of non-colloidal size magnetic particles by adding said particles to a mixture of a viscosity additive in a carrying fluid;

preparing a dispersion of colloidal size magnetic particles with a stabilizer in a carrying fluid;

10 preparing a dispersion of colloidal size polishing particles in a carrying fluid;

mixing said colloidal size magnetic particle dispersion and said colloidal size polishing particle dispersion to form an intermediate mixture;

15 mixing said intermediate mixture with said non-colloidal size magnetic particle dispersion; and

adjusting the pH of said composition to a pH in the range from about 9 to about 12.

51. A method according to claim 50 further comprising the step of mixing a viscosity additive in a carrying fluid prior to the first preparing step.

52. A method according to claim 50 further comprising the step of mixing a stabilizer in a carrying fluid prior to the preparing steps.

53. A method according to claim 50 further comprising the step of adding to the polishing particle dispersion additives to enhance the rate and quality of polishing, said adding step being effected prior to the first mixing step.

54. A method for producing a composition according to claim 39, said method comprising the steps of:

preparing a dispersion of non-colloidal size magnetic particles by adding said particles to a mixture of a viscosity additive in a carrying fluid;

30 preparing a dispersion of colloidal size magnetic particles with a stabilizer in a carrying fluid;



preparing a dispersion of colloidal size polishing particles in a carrying fluid;

adding to the colloidal size polishing particle dispersion at least one oxidizer and at least one inhibitor;

5        mixing said colloidal size magnetic particle dispersion and said colloidal size polishing particle dispersion to form an intermediate mixture;

      mixing said intermediate mixture with said non-colloidal size magnetic particle dispersion; and,

      adjusting the pH of said composition to a pH in the range of about 0.5  
10       to about 5.5.

55. A method for producing a composition according to claim 39, said method comprising the steps of:

      preparing a dispersion of non-colloidal size magnetic particles by adding said particles to a mixture of a viscosity additive in a carrying fluid;

15       preparing a dispersion of colloidal size magnetic particles with a stabilizer in a carrying fluid;

      preparing a dispersion of colloidal size polishing particles in a carrying fluid;

20       adding to the colloidal size polishing particle dispersion at least one inhibitor;

      mixing said colloidal size magnetic particle dispersion and said colloidal size polishing particle dispersion to form an intermediate mixture;

25       mixing said intermediate mixture with said non-colloidal size magnetic particle dispersion to form an intermediate composition;

      adjusting the pH of said intermediate composition to a pH in the range from about 0.5 to about 5.5, if said intermediate composition is not already in that range; and

30       adding at least one oxidizer to the intermediate composition immediately prior to use.

56. A magnetic polishing fluid composition comprising:

colloidal size magnetic particles, wherein said magnetic particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ ;

colloidal size polishing particles, wherein said polishing particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ ;  
at least one stabilizer for stabilizing said colloidal size particles;  
and

a carrying fluid.

57. A composition according to claim 56 further comprising at least one oxidizer.

58. A composition according to claim 57 further comprising at least one inhibitor for controlling the rate of oxidation by said oxidizer.

59. A composition according to claim 57 wherein said colloidal size polishing particles are alumina ( $\text{Al}_2\text{O}_3$ ) particles.

60. A composition according to claim 57 wherein said stabilizer is perchloric acid.

61. A composition according to claim 57 wherein the pH of said composition is in the range from between about 0.5 to about 5.5.

62. A composition according to claim 57 wherein the pH of said composition is in the range from between about 1.5 to about 4.5.

63. A magnetic polishing fluid composition comprising:

colloidal size magnetic particles, wherein said magnetic particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ ;

at least one stabilizer for stabilizing said colloidal size particles;

at least one oxidizer;

at least one inhibitor for inhibiting the rate of oxidation of said oxidizer; and

a carrying fluid;

wherein the pH of said composition is in the range from about 0.5 to about 5.5.

64. A magnetic polishing fluid composition comprising:

colloidal size magnetic particles, wherein said magnetic particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.15  $\mu\text{m}$ ;

colloidal size polishing particles, wherein said polishing particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ ;

at least one stabilizer for stabilizing said colloidal size particles;

at least one oxidizer;

at least one inhibitor for inhibiting the rate of oxidation of said oxidizer; and

a carrying fluid;

wherein the pH of said composition is in the range from about 0.5 to about 5.5.

65. A composition according to claim 64 wherein said colloidal size polishing particles have a weight percent content in said composition ranging from about 1 wt % to about 20 wt %.

66. A composition according to claim 64 wherein said colloidal size magnetic particles have a weight percent content in said composition ranging from about 20 wt % to about 55 wt %.

67. A composition according to claim 64 wherein said at least one stabilizer has a weight percent content in said composition ranging from about 0.5 wt % to about 20 wt %.

68. A composition according to claim 64 wherein said at least one oxidizer has a weight percent content in said composition ranging from about 1 wt % to about 10 wt %.

69. A composition according to claim 64 wherein said at least one inhibitor has a weight percent content in said composition ranging from about 0.01 wt % to about 2 wt %.

70. A composition according to claim 64 wherein said colloidal size magnetic particles, said colloidal size polishing particles, said at least one stabilizer, said at least one oxidizer and said at least one inhibitor have weight percent contents in said composition ranging from about 20 to about 55 wt. %, from about 1 to about 20 weight percent (wt. %), from

0.05 to 20 wt %, from about 1 to about 10 weight percent (wt. %), and from about 0.01 wt % to 2 wt %, respectively.

71. A composition according to claim 64 wherein said colloidal size magnetic particles, said colloidal size polishing particles, said at least one stabilizer, said at least one oxidizer and said at least one inhibitor have weight percent contents in said composition ranging from about 25 to about 35 weight percent (wt. %), from about 3 to about 15 wt. %, from about 1 to about 8 wt. %, from about 2 to about 7 wt. %, and from about 0.03 to about 1.2 wt. %, respectively.

72. A composition according to claim 64 wherein :

said colloidal size magnetic particles comprise colloidal size magnetite ( $\text{Fe}_3\text{O}_4$ ) particles, said particles having a weight percent content in said composition ranging from about 20 to about 55 wt %;

said colloidal size polishing particles comprising colloidal size alumina ( $\text{Al}_2\text{O}_3$ ) particles, said particles having a weight percent content in said composition ranging from about 1 to about 20 wt.%;

said at least one oxidizer comprising  $\text{Fe}(\text{NO}_3)_3$ , said  $\text{Fe}(\text{NO}_3)_3$  having a weight percent content in said composition ranging from about 1 to about 10 wt.%;

said at least one inhibitor comprising  $\text{K}_2\text{Cr}_2\text{O}_7$ , said  $\text{K}_2\text{Cr}_2\text{O}_7$  having a weight percent content in said composition ranging from about 0.01 to about 2 wt.%; said at least one stabilizer comprising perchloric acid, said perchloric acid having a weight percent content in said composition ranging from about 0.5 to about 20 wt.%; and

said carrier fluid, adjusted to a pH in the range of about 0.5 to about 5.5, comprising any remaining wt % of said composition.

73. A composition according to claim 56, wherein:

said colloidal size magnetic particles comprise colloidal size magnetite ( $\text{Fe}_3\text{O}_4$ ) particles having a weight percent content ranging from about 20 to about 55 wt % of said composition;

said colloidal size polishing particles, comprise colloidal size silica (SiO<sub>2</sub>) particles having a weight percent content ranging from about 1 to about 20 wt. % of said composition;

said at least one stabilizer comprising tetramethylammonium hydroxide, said hydroxide having a weight percent content ranging from about 0.05 to about 25 wt. % of said composition; and

said carrier fluid, adjusted to a pH in excess of 9, comprising any remaining wt % of said composition.

74. A composition according to claim 56 wherein said colloidal size magnetic particles have a weight percent (wt %) of said composition ranging from about 20 to about 55 wt. %.

75. A composition according to claim 56 wherein said colloidal size polishing particles have a weight percent (wt %) of said composition ranging from about 1 to about 20 wt. %.

76. A composition according to claim 56 wherein said at least one stabilizer has a weight percent (wt %) of said composition ranging from about 0.05 to about 25 wt. %.

77. A composition according to claim 56 wherein said colloidal size magnetic particles, said colloidal size polishing particles and said at least one stabilizer have weight percents (wt %) of said composition ranging from about 20 to about 55 wt. %, from about 1 to about 20 wt. %, and from 0.05 to about 25 wt. %, respectively.

78. A composition according to claim 56 wherein said colloidal size magnetic particles, said colloidal size polishing particles and said at least one stabilizer have weight percents (wt %) of said composition ranging from about 25 to about 35 wt. %, from about 3 to about 15 wt. % and from about 1 to about 8 wt. %, respectively.

79. A method for preparing a composition according to claim 56, said method comprising the steps of:  
preparing a dispersion of colloidal size magnetic particles with a stabilizer in a carrying fluid;

preparing a dispersion of colloidal size polishing particles in a carrying fluid;

mixing said colloidal size magnetic particle dispersion and said colloidal size polishing particle dispersion to form a mixture; and

5 adjusting the pH of said mixture to about 9 – 12.

80. A method according to claim 79 further comprising the step of mixing said carrier fluid with said stabilizer prior to the first preparing step.

81. A method for preparing a composition according to claim 64, said method comprising the steps of:

10 preparing a dispersion of colloidal size magnetic particles with a stabilizer in a carrying fluid;

preparing a dispersion of colloidal size polishing particles in a carrying fluid;

15 adding to the colloidal size polishing particle dispersion at least one oxidizer and at least one inhibitor;

mixing said colloidal size magnetic particle dispersion and said colloidal size polishing particle dispersion to form a mixture; and

adjusting the mixture to a final pH of about 0.5-5.5.

20 82. A method for preparing a composition according to claim 64, said method comprising the steps of:

preparing a dispersion of colloidal size magnetic particles with a stabilizer in a carrying fluid;

preparing a dispersion of colloidal size polishing particles in a carrying fluid;

25 adding to the colloidal size polishing particle dispersion at least one inhibitor;

mixing said colloidal size magnetic particle dispersion and said colloidal size polishing particle dispersion to form a mixture;

30 adjusting the pH of said mixture to a pH of about 0.5 to about 4.5, if said mixture is not already at that pH; and

adding to the mixture an oxidizer immediately prior to use.

83. A magnetic polishing fluid composition comprising:

non-colloidal magnetic particles, wherein said magnetic particles have a mean particle size range from about 0.15  $\mu\text{m}$  to about 3.0  $\mu\text{m}$ ;

colloidal size polishing particles, said polishing particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ ;

5       at least one stabilizer for stabilizing said colloidal particles;  
      an additive for adjusting viscosity; and  
      a carrying fluid.

84. A composition according to claim 83, wherein:

10       said magnetic particles comprise carbonyl iron particles, said particles having a weight percent content in said composition from about 20 to about 55 wt. %;

      said colloidal size polishing particles comprise colloidal size silica particles, said particles having a weight percent content in said composition from about 1 to about 20 wt. %;

15       said at least one stabilizer comprises tetramethylammonium hydroxide, said hydroxide having a weight percent content in said composition ranging from about 0.5 to about 25 wt. %;

      said additive for adjusting viscosity comprises polyethylene glycol, said glycol having a weight percent content in said composition ranging  
20       from about from about 0.1 to about 10 wt. %; and

      said carrier fluid adjusted to a pH in excess of 9 comprising any remaining wt % of said composition.

85. A composition according to claim 83 wherein said magnetic particles have a weight percent content in said composition ranging from about 20  
25       to about 55 wt. %.

86. A composition according to claim 83 wherein said polishing particles have a weight percent content in said composition ranging from about 1 to about 20 wt. %.

87. A composition according to claim 83 wherein said at least one  
30       stabilizer has a weight percent content in said composition ranging from about 0.5 wt % to about 25 wt %.

88. A composition according to claim 83 wherein said viscosity additive has a weight percent content in said composition ranging from about 0.1 wt % to about 10 wt. %.

89. A composition according to claim 83 wherein said magnetic particles, said polishing particles, said at least one stabilizer and said viscosity additive have weight percent contents in said composition ranging from about 20 to about 55 wt. %, from about 1 to about 20 wt. %, from about 0.5 wt % to about 25 wt % and from about 0.1 wt % to about 10 wt. %, respectively.

90. A composition according to claim 83 wherein said magnetic particles, said polishing particles, said at least one stabilizer and said viscosity additive have weight percent contents in said composition ranging from about 25 to about 35 wt. %, from about 3 to about 5 wt. %, from about 1 wt % to about 8 wt % and from about 1 wt % to about 5. wt %, respectively.

91. A method for producing a composition according to claim 83, said method comprising the steps of:

preparing a dispersion of magnetic particles by adding said particles to a viscosity additive in a carrying fluid;

preparing a colloidal size polishing particle dispersion with a stabilizer in a carrying fluid;

mixing said dispersion of magnetic particles and said dispersion of colloidal size polishing particles; and

adjusting the pH of the mixture to a pH in the range from about 9 to about 12.

92. A method according to claim 91 further comprising the step of mixing a viscosity additive in a carrier fluid prior to the first preparing step.

93. A method according to claim 91 further comprising the step of mixing a stabilizer in a carrier fluid prior to the second preparing step.

94. A composition according to claim 83 further comprising an oxidizer.

95. A composition according to claim 94 further comprising an inhibitor which inhibits the rare of oxidation of the oxidizer.



96. A composition according to claim 94 wherein said colloidal size polishing particles are alumina ( $\text{Al}_2\text{O}_3$ ) particles.
97. A composition according to claim 94 wherein said composition has a pH from about 0.5 to about 5.5.
- 5 98. A composition according to claim 94 wherein said composition has a pH from about 1.5 to about 4.5.
99. A composition according to claim 94 wherein said stabilizer is perchloric acid.
100. A magnetic polishing fluid composition comprising:
- 10 magnetic particles, wherein said non-colloidal magnetic particles have a mean particle size range from about 0.15 to about 3.0  $\mu\text{m}$ ;  
at least one oxidizer;  
at least one inhibitor for inhibiting the rate of oxidation by the oxidizer;  
at least one stabilizer for stabilizing said colloidal particles;  
15 an additive for adjusting viscosity; and  
a carrying fluid;  
wherein the pH of said composition is in a range from between about 0.5 to about 5.5.
101. A magnetic polishing fluid composition comprising:
- 20 magnetic particles, wherein said magnetic particles have a mean particle size range from about 0.15 to about 3.0  $\mu\text{m}$ ;  
colloidal size polishing particles, said polishing particles have a mean particle size range from about 0.01  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ ;  
at least one oxidizer;  
25 at least one inhibitor for inhibiting the rate of oxidation by the oxidizer;  
at least one stabilizer for stabilizing said colloidal particles;  
an additive for adjusting viscosity; and  
a carrying fluid;  
wherein the pH of said composition is in a range from between about  
30 0.5 to about 5.5.
102. A composition according to claim 101 wherein:

said magnetic particles comprise magnetite particles, said particles having a weight percent content in said composition from about 20 to about 55 wt. %;

said colloidal size polishing particles comprise colloidal size alumina particles, said particles having a weight percent content in said composition from about 1 to about 20 wt. %;

said at least one stabilizer comprising perchloric acid, said perchloric acid having a weight percent content in said composition ranging from about 0.5 to about 20 wt. %;

said additive for adjusting viscosity comprising polyethylene glycol, said glycol having a weight percent content in said composition ranging from about 0.1 to about 10 wt. %;

an oxidizer comprising ferric nitrate, said ferric nitrate having a weight percent content in said composition ranging from about 1 to about 10 wt. %;

an inhibitor comprising potassium dichromate, said potassium dichromate having a weight percent content in said composition ranging from about 0.01 to about 2 wt. %; and

said carrier fluid, adjusted to a pH in the range from about 0.5 to about 5.5, comprising any remaining wt % of said composition.

103. A composition according to claim 101 wherein said magnetic particles have a weight percent content in said composition ranging from about 20 to about 55 wt. %.

104. A composition according to claim 101 wherein said colloidal size polishing particles have a weight percent content in said composition ranging from about 1 to about 20 wt. %.

105. A composition according to claim 101 wherein said at least one stabilizer has a weight percent content in said composition ranging from about 0.5 wt. % to about 20 wt. %.

106. A composition according to claim 101 wherein said viscosity adjusting additive has a weight percent content in said composition ranging from about 0.1 wt. % to about 10 wt. %.

107. A composition according to claim 101 wherein said at least one oxidizer has a weight percent content in said composition ranging from about 1 wt. % to about 10 wt. %.
108. A composition according to claim 101 wherein said at least one inhibitor  
5 has a weight percent content in said composition ranging from about 0.01 wt. % to about 2 wt. %.
109. A composition according to claim 101 wherein said magnetic particles, said colloidal size polishing particles, said at least one stabilizer, said viscosity additive, said at least one oxidizer and said at least one inhibitor  
10 have weight percent contents in said composition ranging from about 20 to about 55 wt. %, from about 1 to about 20 wt. %, from about 0.5 wt. % to about 20 wt. %, from about 0.1 wt. % to about 10 wt. %, from about 1 wt. % to about 10 wt. % and from about 0.01 wt. % to about 2 wt. %, respectively.
110. A composition according to claim 101 wherein said magnetic particles,  
15 said colloidal size polishing particles, said at least one stabilizer, said viscosity additive, said at least one oxidizer and said at least one inhibitor have weight percent contents in said composition ranging from about 25 to about 35 wt. %, from about 3 to about 15 wt. %, from about 1 wt. % to about 8 wt. %, from about 1 wt. % to about 5 wt. %, from about 2. wt. % to about 7  
20 wt. % and from about 0.03 wt. % to about 1.2 wt. %, respectively.
111. A method for producing a composition according to claim 101, said method comprising the steps of:
- preparing a dispersion of magnetic particles by adding said particles to a viscosity additive in a carrying fluid;
  - 25 preparing a colloidal size polishing particle dispersion with a stabilizer in a carrying fluid;
  - adding at least one oxidizer and at least one inhibitor to the colloidal size polishing particle dispersion;
  - mixing said dispersion of magnetic particles and said dispersion of  
30 colloidal size polishing particles to form a mixture; and
  - adjusting the pH of said mixture to a pH of about 0.5 to about 5.5.

112. A method according to claim 111 further comprising a step of mixing a viscosity additive with a carrier fluid prior to the first preparing step.

113. A method according to claim 111 further comprising a step of mixing a stabilizer with a carrier fluid prior to the second preparing step.

5 114. A method for producing a composition according to claim 101, said method comprising the steps of:

preparing a dispersion of magnetic particles by adding said particles to a viscosity additive in a carrying fluid;

10 preparing a colloidal size polishing particle dispersion with a stabilizer in a carrying fluid;

adding at least one inhibitor to the colloidal size polishing particle dispersion;

mixing said dispersion of magnetic particles and said dispersion of colloidal size polishing particles to form an intermediate composition;

15 adjusting the pH of the intermediate composition to a pH in the range from about 0.5 to about 5.5 if said composition is not already in that range; and

adding at least one oxidizer to the intermediate composition immediately prior to use.

20 115. A method for producing a composition according to claim 94, said method comprising the steps of:

preparing a dispersion of magnetic particles by adding said particles to a viscosity additive in a carrying fluid;

25 preparing a colloidal size polishing particle dispersion with a stabilizer in a carrying fluid;

adding at least one oxidizer to the colloidal size polishing particle dispersion;

mixing said dispersion of magnetic particles and said dispersion of colloidal size polishing particles to form a mixture; and

30 adjusting the pH of said mixture to a pH of about 0.5 to about 5.5.

116. A method for preparing a composition according to claim 57, said method comprising the steps of:

preparing a dispersion of colloidal size magnetic particles with a stabilizer in a carrying fluid;

preparing a dispersion of colloidal size polishing particles in a carrying fluid;

5 adding to the colloidal size polishing particle dispersion at least one oxidizer;

mixing said colloidal size magnetic particle dispersion and said colloidal size polishing particle dispersion to form a mixture; and

adjusting the mixture to a final pH of about 0.5-4.5.

10 117. A method for producing a composition according to claim 30, said method comprising the steps of:

preparing a dispersion of non-colloidal size magnetic particles by adding said particles to a mixture of a viscosity additive in a carrying fluid;

15 preparing a dispersion of colloidal size magnetic particles with a stabilizer in a carrying fluid;

preparing a dispersion of colloidal size polishing particles in a carrying fluid;

adding to the colloidal size polishing particle dispersion at least one oxidizer;

20 mixing said colloidal size magnetic particle dispersion and said colloidal size polishing particle dispersion to form an intermediate mixture;

mixing said intermediate mixture with said non-colloidal size magnetic particle dispersion; and,

25 adjusting the pH of said composition to a pH in the range of about 0.5 to about 5.5.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IL00/00261

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C09G 1/02  
US CL : Please See Extra Sheet.  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 51/293, 307, 308, 309; 451/93; 252/62.51R, 62.52, 62.56, 62.55, 62.51C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,019,994 A (KELLEY) 26 April 1977, whole document.	38, 63, 100
A	US 5,228,886 A (ZIPPERIAN) 20 July 1993, whole document.	56-49, 54-116
A	US 5,702,630 A (SASAKI et al) 30 December 1997, whole document.	38-49, 54-116
A	US 5,804,095 A (JACOBS et al) 08 September 1998, whole document.	83-116

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
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## INTERNATIONAL SEARCH REPORT

International application No.  
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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A ----- X ----- Y	US 5,578,238 A (WEISS et al) 26 November 1996, col. 5, line 13- col. 7, line 37 and col. 12, line 30-col. 15, line 40.	38-55,57- 72,81,82,94- 116 ----- 56,83 ----- 73-80, 84-93

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INTERNATIONAL SEARCH REPORT

International application No.  
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A. CLASSIFICATION OF SUBJECT MATTER:  
US CL :

51/293, 307, 308, 309; 451/93; 252/62.51R, 62.52, 62.56, 62.55, 62.51C

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